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SUPPLEMENTARY INFORMATION
SOLUBILITY AND NUCLEATION OF METHYL STEARATE AS A FUNCTION OF CRYSTALLISATION ENVIRONMENT

Diana M. Camacho[a*], Kevin J. Roberts[a], Iain More[b], Ken Lewtas[b,c]

[a] School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

[b] Infineum UK Ltd, Milton Hill Business and Technology Centre, Abingdon, OX13 6BB, UK

[c] Current address: Lewtas Science & Technologies Ltd., Oxford, OX2 7DY, UK

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*Corresponding author

ABSTRACT

Additional and more detailed materials are provided as a supplement to the paper with the above title. It includes:

1. Comparative schemes for the isothermal or the polythermal method based on a concentration vs temperature profile
2. The full derivation of the set of expressions that comprise the $KBHR$ approach [1, 2]
3. Kerosene n-alkanes chain length distribution
4. Temperature calibration lines for the Crystal 16 unit
5. Flow chart describing how to apply the KBHR approach for the analysis of nucleation kinetics from polythermal experimental data
6. Experimental crystallisation T_c and dissolution T_{diss} temperatures as a function of cooling rate q
7. Comparative figures of nucleation kinetics parameters for methyl stearate crystallising from dodecane, kerosene and toluene solvents at the experimental crystallisation temperatures

The reference numbering in the supplementary information coincides with that in the paper. The reference to equations numbering from section 3 to 7 coincides with that in the paper.

1. Comparative schemes for the isothermal or the polythermal method based on a concentration vs temperature profile

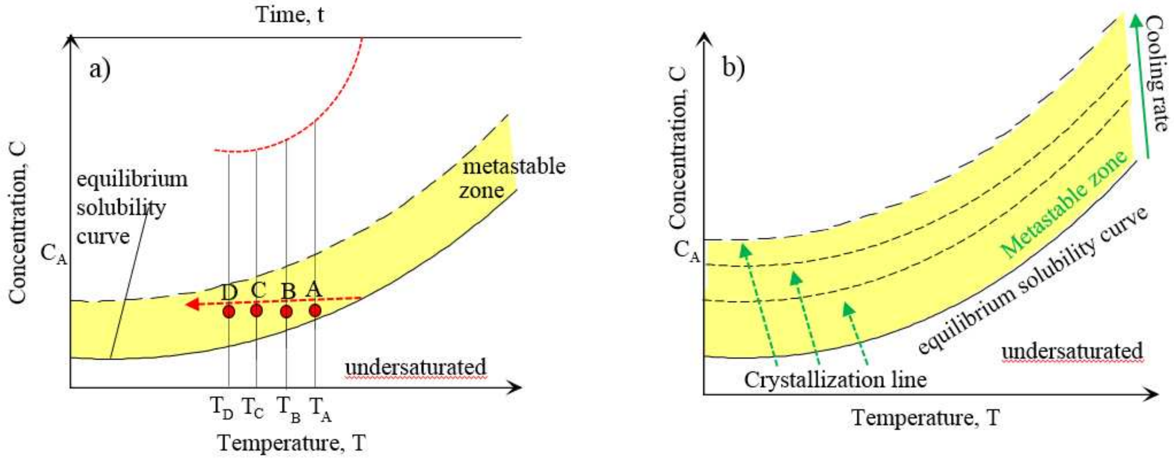

Fig. S1 Comparative scheme of the different approaches used to collect experimental data to assess nucleation kinetics based on a concentration vs temperature plot a) isothermal b) polythermal

2. Detailed derivation of the model equations, used to assess solution's crystallisation kinetics, from the Kolmogorov-Johnson-Mehl-Avrami ($KJMA$) expression

A detailed derivation of the set of expressions that conforms the $KBHR$ approach is presented below. Expressions for the dependence of critical undercooling on cooling rate are derived for the cases of progressive PN and instantaneous nucleation IN mechanism from the Kolmogorov-Johnson-Mehl-Avrami $KJMA$.

The $KBHR$ approach makes use of a master equation presented by Kashchiev [37] that describes the first-order transition nucleation process restricted to one component nucleation by either homogeneous or heterogeneous nucleation.

In crystallisation of a single component the phase transformation kinetics can be explained by the Kolmogorov-Johnson-Mehl-Avrami $KJMA$ equation [37]. The central idea of this equation is to focus on the increment in the fraction transformed and to relate it to the current value of the fraction transformed. A conversion fraction of the crystallites´ volume α is typically defined as

$$\alpha = \frac{V_c}{V} \tag{1}$$

where V_c is the volume of crystallites and V the total volume of solution

Estimating the dependence of the volume of crystallites on time $V_c(t)$ from the master equation is a complex mathematical challenge especially at the late stages of crystallisation when multiple contacts between crystallites should be considered. To overcome this difficulty the $KJMA$ theory assumes that V_c results from nucleation of material points at a rate $J(t)$ which then only expand irreversibly in radial direction with growth rate $G(t)$ [37].Under this assumption V_c can be easily found at the early stage of crystallisation not long after the initial moment $t = 0$ when there is already a certain level of supersaturation, the whole volume of the solution is available for nucleation and there is no contact between the growing crystallites.

The obtained $KJMA$ formula limited to the early stage of nucleation shows that the progression of the fraction of crystallised volume is controlled by two basic parameters of the process of crystallisation: crystallite nucleation and growth rates [1, 2, 37].

2.1 Progressive nucleation case

In the case of progressive nucleation the $KJMA$ formula can be expressed as [2, 37]

$$\alpha(t) = k_v \int_0^t J(t') \left[\int_0^{t-t'} G(t'')dt'' \right]^d dt^{\acute{}} \quad for\ \alpha < 0.1 \tag{2}$$

where t and t' are time integration variables, J is the time dependent rate of either homogeneous or heterogeneous nucleation, G is the time dependent radial crystallites´ growth rate, $d = 1,2,3$ is the dimensionality of crystallites´ growth i.e. 3 for spheres or cubes, 2 for disk or plates and 1 for needle shaped crystals, k_v (m^{3-d}) crystallites´ growth shape factor i.e. $\frac{4\pi}{3}$ for spheres, 8 for cubes, πH_0 for disks, $4H_0$ for square plates (H_0 is the fixed disk or plate thickness), and $2A_0$ for needles (A_0 is the fixed needle cross-sectional area)

Starting at $t = 0$ from the equilibrium temperature T_e at steady cooling, relative undercooling is defined as

$$u = \frac{\Delta T}{T_e} = \frac{T_e - T}{T_e} \tag{3}$$

where T is the solution's temperature

From classical $3D$ nucleation theory the rate of crystallites nucleation can be expressed in terms of relative undercooling as

$$J(t) = K_J e^{\frac{-b}{(1-u)u^2}} \tag{4}$$

where K_J is the nucleation rate constant and the dimensionless thermodynamic parameter b is given by

$$b = \frac{k_n v_o^2 {\gamma_{eff}}^3}{kT_e\lambda^2} \tag{5}$$

where k_n is the nuclei numerical shape factor i.e. $16\pi/3$ for spherical nuclei and 32 for cubic nuclei, v_o is the volume occupied by a solute molecule in the crystal, γ_{eff} is the effective interfacial tension of the crystal nucleus, λ is the molecular latent heat of crystallisation and k is the Boltzmann constant

In the same way the radial crystallite growth rate $G(t)$ in terms of undercooling can be expressed as

$$G(t) = m\left(\frac{T_e}{q}\right)^{m-1} K_G^m \left[1 - e^{\frac{-au}{(1-u)}}\right]^{nm} u^{m-1} \tag{6}$$

where K_G is the crystal growth rate constant and n and $m > 0$ crystallites' growth exponents. $n = 1$ for growth mediated by diffusion of solute and $n = 2$ growth controlled by the presence of screw dislocations in the crystallite. m ranges between ½ and 1. $m = 1/2$ for growth controlled by undisturbed diffusion of solute and $m = 1$ for growth by diffusion of solute through a stagnant layer around the crystal and normal or spiral growth limited by transfer of solute across the crystal/solution interface. At $m = 1$ the crystallite radius increases linearly with time [2, 37] and the dimensionless latent heat of crystallisation

$$a = \frac{\lambda}{kT_e} \tag{7}$$

Inserting equation (4) and (6) in equation (2) and defining $t' = \left(\frac{T_e}{q}\right)x$ and $t^{''} = \left(\frac{T_e}{q}\right)z$, α can be expressed in terms of undercooling

$$\alpha(u) = C_{m,d} \int_0^u e^{\frac{-b}{(1-x)x^2}} \left(\int_0^{u-x} z^{m-1} \left[1 - e^{\frac{-az}{(1-z)}} \right]^{nm} dz \right)^d dx \tag{8}$$

where the dimensionless parameter $C_{m,d}$ is given by

$$C_{m,d} = k_v m^d K_J K_G^{md} \left(\frac{T_e}{q} \right)^{md+1} \tag{9}$$

Equation (8) can be solved if the analysis is restricted to small enough values of u satisfying inequalities

$$u < 0.1, au < 1 \tag{10}$$

then

$$1 - u \approx 1 \text{ and } 1 - e^{\frac{-au}{(1-u)}} \approx au \tag{11}$$

With these simplifications equation (8) then becomes

$$\alpha(u) = C_{m,d}a^{nmd}\int_0^u e^{\frac{-b}{x^2}}\left[\int_0^{u-x} z^{(n+1)m-1}dz\right]^d dx \tag{12}$$

Likewise, it has been shown [1, 2] that the inner integral in equation (12) can be solved for small values of u, satisfying

$$u < \left(\frac{2b}{3}\right)^{1/2} \tag{13}$$

leading to

$$\alpha(u) = K_{m,d}\left(\frac{u^3}{2b}\right)^{(n+1)md+1} e^{\frac{-b}{u^2}} \tag{14}$$

Additionally, it was observed [2] that the exponential term in the above equation is an approximate of $e^{\frac{-b}{(1-u)u^2}}$ and thus equation (14) becomes

$$\alpha(u) = K_{m,d}\left(\frac{u^3}{2b}\right)^{(n+1)md+1} e^{\frac{-b}{(1-u)u^2}} \tag{15}$$

where the dimensionless parameter $K_{m,d}$ is given by

$$K_{m,d} = \frac{\Gamma[(n+1)md+1]}{(n+1)^d}k_v a^{nmd}K_J K_G^{md}\left(\frac{T_e}{q}\right)^{md+1} \tag{16}$$

and Γ is the gamma function

Equation (15) can be expressed in terms of the number of crystallites upon replacing α by N and setting $d = 0$

$$N(u) = K_N \left(\frac{u^3}{2b}\right) e^{\left[\frac{-b}{(1-u)u^2}\right]} \tag{17}$$

where K_N is obtained by making $K_N = K_{m,0}$ and is given by

$$K_N = \frac{V K_J T_e}{q} \tag{18}$$

If plots of α and N are constructed as a function of u, they show that α and N are monotonically increasing functions of u, with a sharp rise at a certain value that corresponds to the relative critical undercooling for crystallisation u_c [2] defined as

$$u_c = \frac{\Delta T_c}{T_e} \tag{19}$$

where

$$\Delta T_c = T_e - T_c \tag{20}$$

Here T_c is the crystallisation temperature

For $u < u_c$ crystallites are so small or few that α and N cannot be detected or are below the detection limit α_{det}, N_{det} . For $u > u_c$ the solution will contain big enough crystallites that α

and N will be detected $\alpha > \alpha_{det}$ and $N > N_{det}$. This means u_c is the maximum relative undercooling that a solution can sustain without detectable crystallisation. In other words, u_c represents the solution metastability limit in terms of undercooling [1,2]. This limit, however, depends on a number of parameters among which one of the most featured is the cooling rate (q). With the help of the previously presented equations for α and N, the $u_c(q)$ dependence can be determined.

Expressing equation (17) it in terms of u_c gives

$$N(u_c) = N_{det} = \frac{VK_JT_e}{q}\left(\frac{{u_c}^3}{2b}\right)e^{\left[\frac{-b}{(1-u_c){u_c}^2}\right]} \tag{21}$$

Upon taking logarithms at both sides of equation (21) a model expression that relates relative critical undercooling u_c with cooling rate q is obtained

$$ln\, q = ln\frac{VK_JT_e}{N_{det}\, 2b} + 3\, ln\, u_c - \frac{b}{(1-u_c){u_c}^2} \tag{22}$$

Likewise, if the parameters q_0 , a_1 and a_2 are defined by

$$a_1 = 3 \tag{23}$$

$$a_2 = b \tag{24}$$

$$q_0 = \frac{VK_JT_e}{N_{det}\, 2b} \tag{25}$$

Then the latter equation becomes

$$ln\, q = ln\, q_0 + a_1\, ln\, u_c - \frac{a_2}{(1-u_c){u_c}^2} \tag{26}$$

When equation (26) is derived by means of α, the parameters q_0 , a_1 and a_2 are defined by

$$a_1 = 3 + \frac{3nmd}{md+1} \tag{27}$$

$$a_2 = \frac{b}{md+1} \tag{28}$$

$$q_0 = T_e \left\{ \frac{\Gamma[(n+1)md+1]K_v a^{nmd} K_J K_G^{md}}{(n+1)^d\, (2b)^{(n+1)md+1} \alpha_{det}} \right\}^{\frac{1}{(md+1)}} \tag{29}$$

The parameters in equation (26) $\ln q_0$, a_1 and a_2 have a physical meaning. a_1 has a relation with the crystallites growth as its values are determined by the growth exponents n, m and d. a_2 is proportional or equal to the thermodynamic nucleation parameter b and q_0 has a relation with parameters of both nucleation and crystallite growth processes.

2.2 Instantaneous nucleation case

In the case of instantaneous nucleation IN a similar derivation was done [1] but taking into account that for the case of IN all crystallites nuclei appear at once with a concentration C_o at the moment t_o. Thus the change of the volume of crystallites with time will only depend on the crystallites´ growth and can be expressed as

$$\alpha(t) = k_v C_o \left[\int_{t_0}^{t} G(t')\, dt'\right]^d \tag{30}$$

Where t' time integration variables, $d = 1{,}2{,}3$ dimensionality of crystallite´s growth, k_v (m^{3-d}) crystallite´s growth shape factor.

Using equation (6) and setting $t' = \frac{T_e}{q} x$ an expression for α in terms of u can be found

$$\alpha(u) = C_{m,d} \left(\int_{u}^{u} x^{m-1} \left[1 - e^{\frac{-ax}{(1-x)}}\right]^{nm} dx\right)^d \tag{31}$$

where the dimensionless parameter $C_{m,d}$ is given by

$$C_{m,d} = k_v m^d C_o \left(\frac{K_G T_e}{q}\right)^{md} \tag{32}$$

For small enough undercooling

$$u < 0.1, au < 1 \tag{33}$$

in which case

$$1 - u \approx 1 \text{ and } 1 - e^{\frac{-au}{(1-u)}} \approx au \tag{34}$$

The integral in equation (31) can be solved leading to

$$\alpha\ (u) = K_{m,d}\left[u^{(n+1)m} - u_o^{(n+1)m}\right]^d \tag{35}$$

In this expression u_o is the relative undercooling at the time t_o and is given by

$$u_o = \frac{\Delta T_o}{T_e} = \frac{qt_0}{T_e} \tag{36}$$

Here ΔT_o is defined by

$$\Delta T_0 = T_e - T_0 \tag{37}$$

where T_o is the solution temperature at the time t_o

Likewise, $K_{m,d}$ is given by

$$K_{m,d} = \frac{k_v C_o \left(\frac{a^n K_G T_e}{q}\right)^{md}}{(n+1)^d} \tag{38}$$

As in the case of progressive nucleation α is a monotonically increasing function of u [1] with a sharp rise at a certain value that corresponds to the relative critical undercooling u_c .

Therefore defining $\alpha(u_c) = \alpha_{det}$ and taking logarithms at both sides of equation (35), an expression can be obtained for the dependence of relative critical undercooling on cooling rate

$$\ln q = \ln q_0 + \left(\frac{1}{m}\right) \ln\left[u_c^{(n+1)m} - u_0^{(n+1)m}\right] \tag{39}$$

In this expression $u_0 \geq 0$, $u_c > u_o$ and the parameter q_0 is given by

$$q_o = \left[\frac{k_v C_o}{(n+1)^d \alpha_{det}}\right]^{\frac{1}{md}} a^n K_G T_e \tag{40}$$

If additionally, the undercooling at which all nuclei spontaneously appear is small enough so that

$$u_o^{(n+1)m} \ll u_c^{(n+1)m} \tag{41}$$

Equation (39) takes the form of a straight line given by

$$\ln q = \ln q_o + (n+1) \ln u_c \tag{42}$$

It should be noted that a comparison of equation (39), with the one obtained for PN derived by means of α, which is defined as

$$ln\, q = ln\, q_0 + \left(3 + \frac{3nmd}{md+1}\right) ln\, u_c - \frac{a_2}{(1-u_c)u_c^2} \tag{43}$$

shows how the dependence of the relative critical undercooling u_c on the cooling rate q is different depending of the mechanism by which nucleation takes place. In the case of PN the expression contains parameters depending on both crystallites nucleation and growth whereas in the case of IN the parameters in the expression are only related to the crystallite´s growth.

2.3 The nucleation rate *J*

The nucleation rate J given by expression (4) equates that given by 3D classical nucleation theory expressed in terms of relative critical undercooling u.

The classical theory equation for nucleation is given by expression (44)

$$J = K_J \exp -\left[k_n v_o^2 \gamma_{eff}^3 / (kT)^3 (ln\, S)^2\right] \tag{44}$$

Due to the drop of T during cooling, J changes primarily because of the strong temperature dependence of the exponential factor. In this factor, C_e is an exponential function of T which can be approximated by the integrated van’t Hoff equation

$$C_e(T) = C_r e^{\frac{-\lambda}{kT}}. \tag{45}$$

Here the reference solute concentration C_r and the molecular latent heat of crystallisation λ are weak functions of temperature and can be treated as T-independent. Since T and C equal their equilibrium values T_e and C_e when cooling commences according to equation (45) we have

$$C = C_r exp\left(\frac{-\lambda}{kT_e}\right) \tag{46}$$

and hence

$$\frac{C}{C_e} = exp\left(\frac{\lambda\Delta T}{kT_e T}\right) \tag{47}$$

where $\Delta T = T_e - T$ is the undercooling.

Thus combining equation (44) and (47) yields

$$J = K_J \exp\left[\frac{-b}{\left(\frac{1-\Delta T}{T_e}\right)\left(\frac{\Delta T}{T_e}\right)^2}\right] \tag{48}$$

where the dimensionless thermodynamic parameter b is given by equation (5)

3. Kerosene n-alkanes chain length distribution

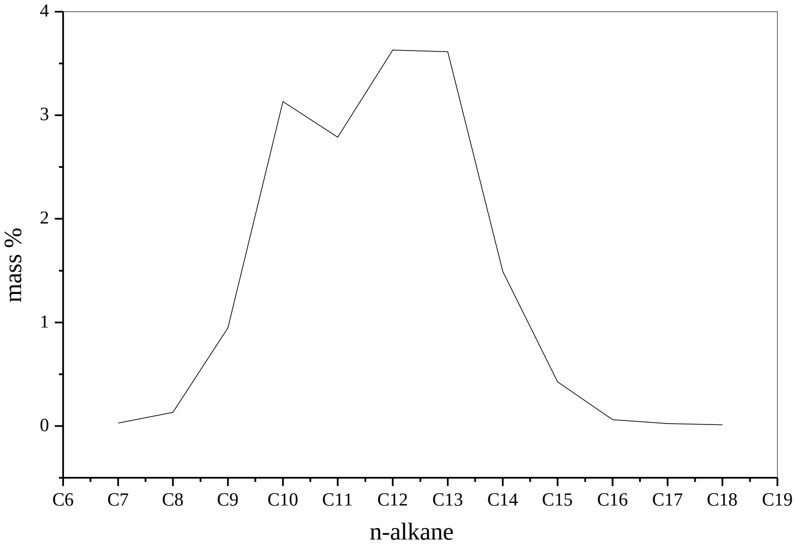

Fig. S2 Kerosene n-alkane mass fraction distribution as obtained by 2D Gas Chromatography analysis performed by Infineum UK

4. Temperature calibration lines for the Crystal 16 unit

Temperature calibration lines for dodecane, kerosene and toluene solvents are provided below. These are obtained by plotting the temperature at which the Crystal 16® is programmed against the actual temperature of the solvent as measured by a calibrated thermocouple.

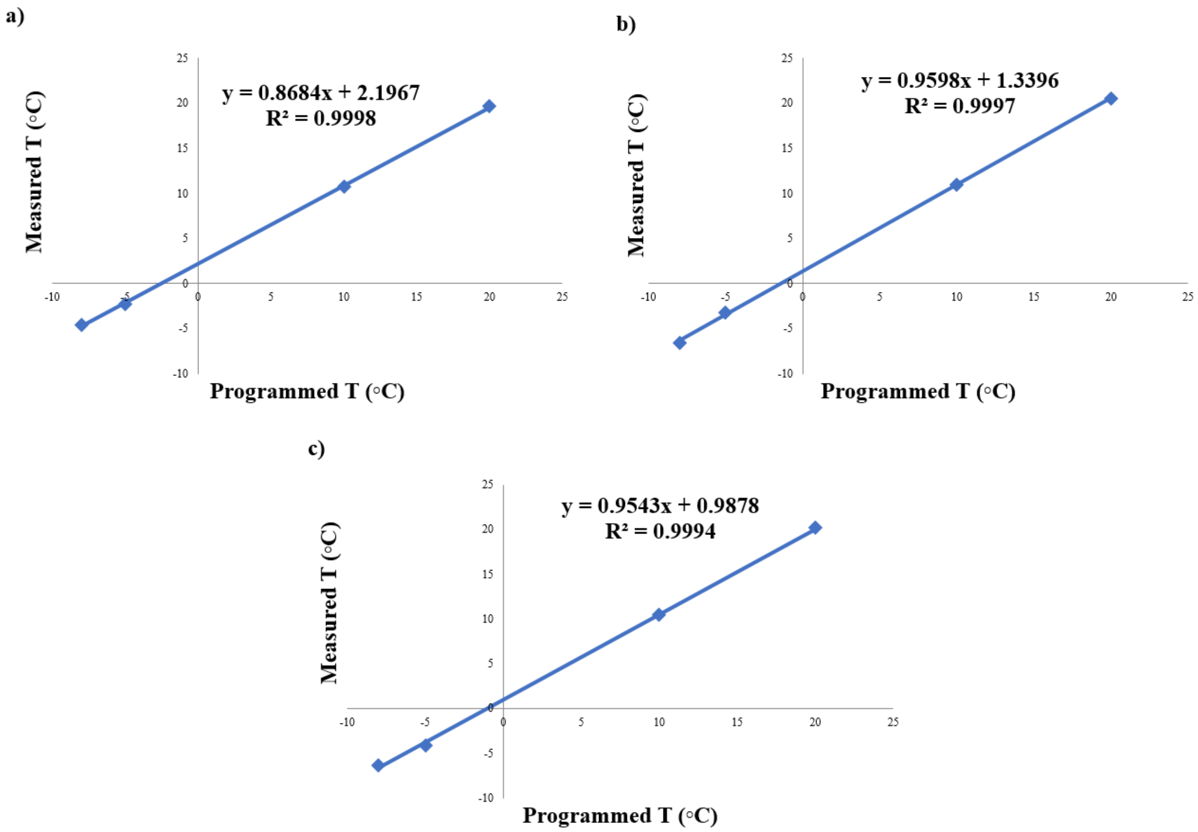

Fig. S3 Temperature calibration for the Crystal 16 unit for a) dodecane, b) kerosene and c) toluene solvents

5. Flow chart describing how to apply the KBHR approach for the analysis of nucleation kinetics from polythermal experimental data

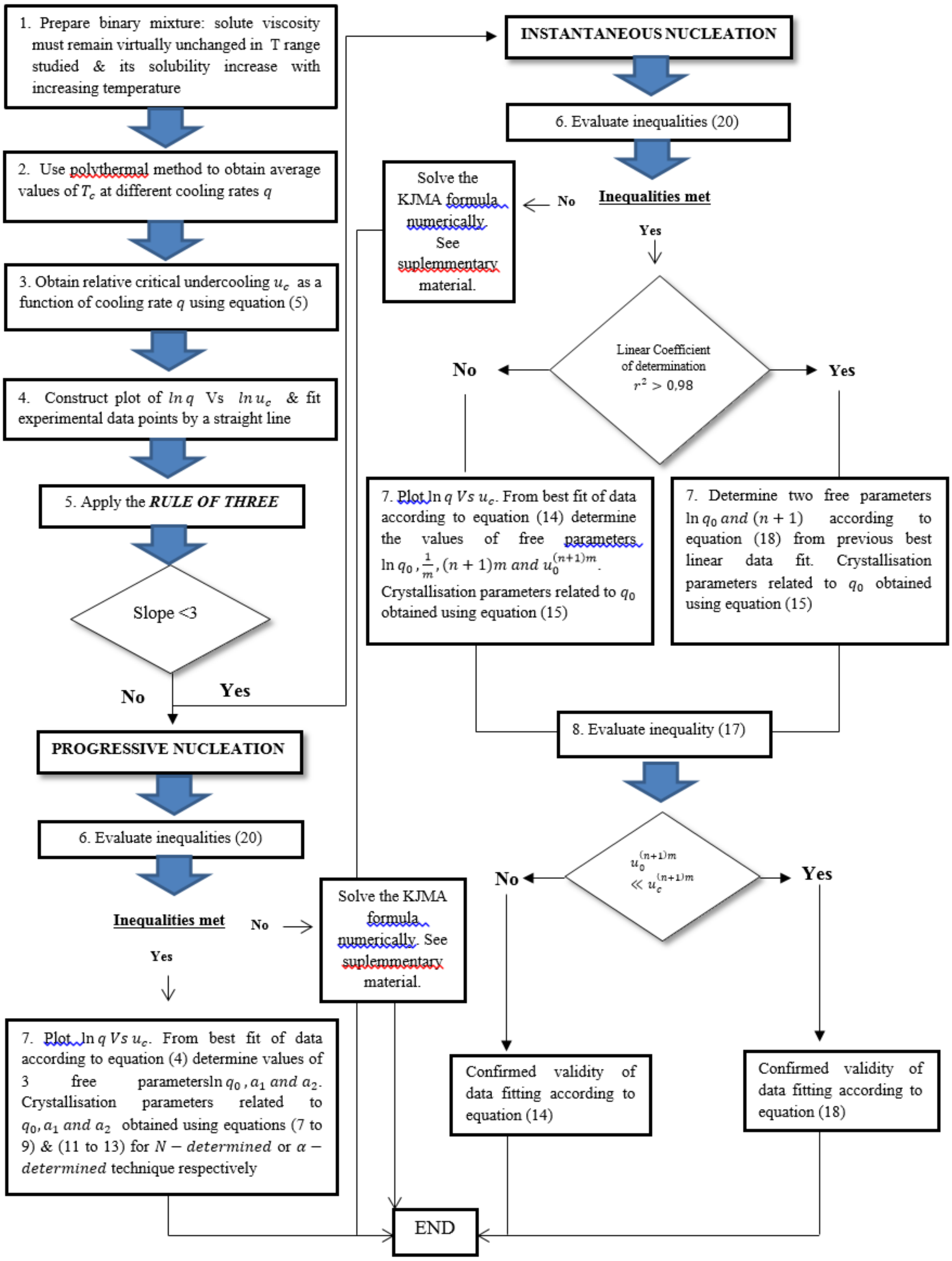

Fig. S4 Flowchart describing the procedure to follow in order to apply ($KBHR$) approach for the interpretation of metastable zone width data ($MSZW$) collected by means of the polythermal method

6. Experimental crystallisation T_c and dissolution T_{diss} temperatures as a function of cooling rate q

Table S1. Average dissolution (T_{diss}) and crystallisation (T_c) temperatures as a function of cooling rate for methyl stearate in dodecane, kerosene and toluene at solution concentrations 200, 250, 300 and 350 g/L of solvent for the first two solvents and 154, 192, 231 and 269 g/L of solvent for toluene. Standard deviation (SD) of crystallisation and dissolution temperatures. Relative critical undercooling u_c calculated according to equation (5). Equilibrium temperatures T_e obtained from extrapolation of best-fit straight lines through $T_{diss}(q)$ data points

Rate °C /min	T_c (°C)	SD T_c (°C)	T_{diss} (°C)	SD T_{diss} (°C)	u_c
dodecane					
200					
0.25	15.81	0.19	19.67	0.11	0.010
1	15.03	0.10	20.71	0.10	0.013
3.2	13.61	0.48	23.47	0.26	0.017
9	10.86	0.04	35.37	0.10	0.027
			T_e= 18.70		
250					
0.25	17.43	0.28	22.19	0.10	0.012
1	16.82	0.36	22.80	0.10	0.015
3.2	15.45	0.30	25.30	0.33	0.019
9	12.88	0.55	36.36	0.41	0.028
			T_e= 21.09		
300					
0.25	18.84	0.26	23.04	0.11	0.011
1	18.56	0.13	23.94	0.20	0.012
3.2	17.15	0.18	26.29	0.22	0.017
9	14.56	0.31	36.72	0.10	0.026
			T_e= 22.18		
350					
0.25	19.76	0.14	24.18	0.10	0.015
1	19.18	0.26	25.49	0.26	0.017
3.2	17.90	0.21	29.22	1.02	0.021
9	14.67	0.43	36.85	0.06	0.032
			T_e= 24.12		
Kerosene					
200					
0.25	12.43	0.66	17.66	0.07	0.017
1	11.76	0.96	18.67	0.09	0.019
3.2	10.11	0.59	22.11	0.15	0.025
9	7.66	0.38	30.75	0.49	0.033
			T_e=17.25		
250					
0.25	15.37	0.47	19.54	0.05	0.013
1	14.85	0.50	20.67	0.11	0.015
3.2	12.24	0.54	24.59	0.36	0.024

9	9.98	0.50	33.47	0.63	0.032
			T_e= 19.21		
300					
0.25	16.73	0.45	21.03	0.04	0.014
1	15.53	0.46	22.34	0.17	0.018
3.2	13.91	0.36	27.02	0.46	0.024
9	11.24	0.35	36.01	0.97	0.033
			T_e= 20.86		
350					
0.25	17.81	0.56	22.19	0.11	0.014
1	16.95	0.16	23.65	0.23	0.017
3.2	15.28	0.57	28.18	0.73	0.023
9	11.90	0.07	37.58	1.09	0.034
			T_e= 22.01		
Toluene					
154					
0.25	-2.39	1.48	2.17	0.09	0.016
0.5	-3.69	1.56	2.42	0.19	0.020
1	-3.02	0.92	3.01	0.18	0.018
1.5	-4.11	1.08	3.51	0.05	0.022
			T_e= 1.90		
192					
0.25	-0.10	1.79	4.48	0.11	0.016
0.5	-0.65	1.02	5.09	0.07	0.018
1	-0.83	1.46	5.47	0.12	0.019
1.5	-1.42	0.93	5.97	0.14	0.021
			T_e= 4.36		
231					
0.25	1.06	1.16	6.20	0.09	0.018
0.5	0.78	0.96	7.13	0.09	0.019
1	0.30	1.07	7.71	0.09	0.018
1.5	0.13	0.63	8.39	0.09	0.022
			T_e= 6.04		
269					
0.25	2.92	0.50	7.69	0.10	0.016
0.5	3.03	0.46	8.79	0.10	0.016
1	2.34	0.55	9.39	0.10	0.018
1.5	1.85	0.61	10.26	0.08	0.020
			T_e= 7.50		

7. Comparative plots of nucleation kinetic parameters for methyl stearate crystallising from dodecane, kerosene and toluene solvents

Fig. S5 shows the results for each of the nucleation parameters obtained as a function of solvent and solution concentration at the corresponding experimental crystallisation temperatures i.e. the crystallisation temperatures obtained from the extrapolated lines to 0°C/min for the dependence of crystallisation temperature (T_c) on cooling rate (q), at each of the chosen solutions' concentrations.

Given that these plots are not obtained at iso-supersaturation values they can be used to perform only an initial screening of the behaviour of methyl stearate nucleation as a function of crystallisation environment. From the engineering point of view Fig S5. shows practically the impact of solution environment on nucleation parameters at the experimental crystallisation temperatures e.g. that interfacial tensions are higher in toluene, which has a direct impact on the nucleation rates in this solvent where they are the lowest.

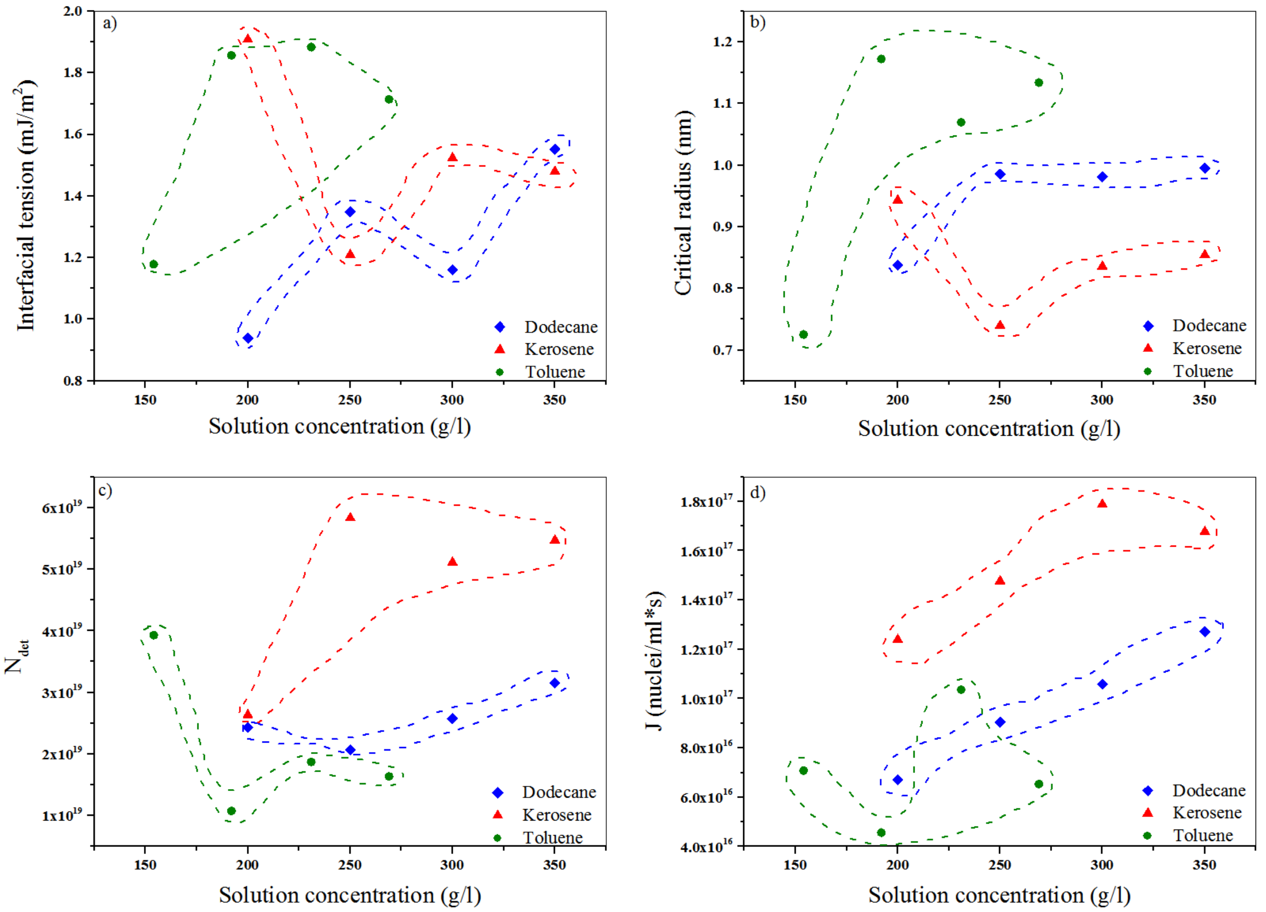

Fig. S5 Comparison of nucleation kinetics parameters for methyl stearate crystallising from dodecane, kerosene and toluene solvents at different solution concentrations. a) interfacial tension γ; b) critical radious r^*; c) number of crystals at the detection point N_{det} and d) nucleation rates J